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**Qingjiang Chen, Asker Aarkrog, Sven P. Nielsen, Henning Dahl-
gaard, H. Nies, Yixuan Yu, K. Mandrup**

**Risø National Laboratory, Roskilde, Denmark
February 1991**

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DETERMINATION OF PLUTONIUM IN ENVIRONMENTAL SAMPLES BY CONTROLLED
VALENCE IN ANION EXCHANGE

Qingjiang Chen*, Asker Aarkrog, Sven P. Nielsen, Henning
Dahlggaard, H. Nies**, Yixuan Yu*, K. Mandrup

*Institute of Atomic Energy, Beijing, China

** Deutsches Hydrographisches Institut, Hamburg, Germany

Abstract. The method was successfully used for collecting $^{239,240}\text{Pu}$ from 200 litres seawater by coprecipitation with 16 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ under reducing conditions without filtering. The plutonium is leached by concentrated HNO_3 + HCl from the coprecipitate and the solid particles. The precipitate is heated at 400°C and digested in aqua regia. Na_2SO_3 and NaNO_2 have been applied to obtain Pu^{4+} valence in 0.5-1 N HNO_3 for different samples. Plutonium and thorium are coabsorbed on anionic resin from 8 N HNO_3 . The column is eluted with 8 N HNO_3 containing fresh NaNO_2 to keep Pu^{4+} valence for uranium decontamination. The system of the column is changed from 8 N HNO_3 to concentrated HCl with 50 ml conc. HCl containing a few milligram NaNO_2 . Further decontamination of thorium was achieved by elution with concentrated HCl instead of 9 N HCl . The plutonium is successfully stripped by H_2O , NaOH , 2 N HNO_3 and 0.5 N HNO_3 containing 0.01 M NaNO_3 . The chemical yield of plutonium for a 200 litres-seawater sample is 60-80%. The resolution of the electroplated thin source is very good.

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1. INTRODUCTION

Previous works^{1,2} have demonstrated that an anion exchange separation of plutonium could be used for routine analysis of environmental samples. The procedures based on the absorption of anionic complexes of plutonium from nitric and hydrochloric acid media have been reviewed¹. The $\text{Pu}(\text{NO}_3)_6^{-2}$ and PuCl_6^{-2} are absorbed on the anionic exchange. However, the plutonium valence ($\text{Pu}^{3,4,5,6}$) is variable. The Pu^{3+} is easily oxidized to Pu^{4+} with NaNO_2 and H_2O_2 , while $\text{Pu}^{5,6+}$ are reduced to Pu^{4+} with NaNO_2 , but the reaction is slow and incomplete. Especially for large volumes seawater samples with organic material and impurities, we found that it was very difficult to control the plutonium valence with NaNO_2 and H_2O_2 . The chemical yield of plutonium was low too. We further observed a thorium contamination in case of large volume seawater eluted by 9 N HCl. Hence it was important to develop a new method to control the plutonium valence and improve the thorium decontamination for large volume seawater and environmental samples.

2. FLOW SHEET OF THE PROCEDURE FOR 200 LITRES SEAWATER

On board the ship:

- 1 1) Acidify 200 litres seawater to pH about 2 with 200 ml concentrated HCl.
- 2) Add 16 g $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, ^{242}Pu and 200 g $\text{Na}_2\text{S}_2\text{O}_5$. Stir by air bubbling for 1 h to reduce all Pu valences to Pu^{3+} .
- 3) Basify the 200 litres seawater to pH = 8.5-9 with diluted NaOH (0.5-1 N) to precipitate $\text{Fe}(\text{OH})_2$. The diluted NaOH is added with a shower to reduce formation of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$.
- 4) Let stay for 5 h or overnight. Siphon off the supernatant liquid to get about 5 litres of $\text{Fe}(\text{OH})_2$ slurry.
- 5) Acidify the solution to about 0.1 N HCl with concentrated HCl (10 ml HCl/litre).
- 6) Transfer the sample to laboratory for analysis.

In the laboratory:

2.
 - 1) Add $\text{Na}_2\text{S}_2\text{O}_3$ (2 g/litre) to the sample solution. Let stay for 1 h.
 - 2) Slowly add diluted NaOH with a small shower to $\text{pH} = 8.5$ to prevent formation of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$. Let stay for 30 min.
 - 3) Siphon off the supernatant liquid. Filter the precipitate with glass filter paper AG/A. Discard the solution.
 - 4) Dissolve the $\text{Fe}(\text{OH})_2$ with 100 ml conc. HCl and 100 ml conc. HNO_3 .
 - 5) Filter the solution through glass filter paper AG/A into a 500 ml beaker. Evaporate to complete dryness.

3.
 - 1) Heat at 400°C for 1 h. Let stay for cooling. Add 120 ml aqua regia to dissolve. Cover the beaker with a glass disc, heat for 1 h.
 - 2) Evaporate to dryness. Repeat step 1). Filter the solution. Wash the precipitate with 100 ml 8 N HNO_3 . Discard the precipitate.
 - 3) Evaporate to about 7 ml. Dilute to 150 ml. The acid is about 0.5-1 N HNO_3 .
 - 4) Add 3 g Na_2SO_3 . Let stay for 20 min. The plutonium is reduced to Pu^{+3} .
 - 5) Add 3 g NaNO_2 . Let stay for 10 min. The Pu^{+3} is oxidized to Pu^{+4} .
 - 6) Acidify the solution to 8 N HNO_3 with 165 ml concentrated HNO_3 .

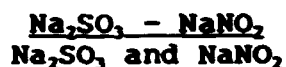
4.
 - 1) Add the solution to a column (10 x 2.1 cm AG 1- X_4 , 100-200 mesh) which is equilibrated with 50 ml 8 N HNO_3 + 1 g $\text{K}_2\text{S}_2\text{O}_8$ and 100 ml 8 N HNO_3 + 0.5 g NaNO_2 (fresh). The flow rate is about 3 ml/min.
 - 2) Wash the column with 350 ml 8 N HNO_3 (10c.v) + 1 g NaNO_2 (fresh).
 - 3) Wash with 50 ml concentrated HCl which is saturated with 100 mg NaNO_2 (fresh).
 - 4) Wash with 300 ml concentrated HCl .

5.
 - 1) Strip with: 30 ml H_2O , 20 ml 0.3 N NaOH, 30 ml H_2O , 20 ml 2 N HNO_3 , 200 ml 0.5 N HNO_3 containing 0.01 M NaNO_3 . Evaporate to dryness.
 - 2) Dissolve the precipitate with 10 ml 0.7 N HNO_3 . Add 300 mg Na_2SO_3 . Stir and let stay for 15 min. Add 300 mg NaNO_2 . Let stay for 10 min. Add 12 ml conc. HNO_3 .
 - 3) Make a column (7 x 0.8 cm) Ag 1-X, 100-200 mesh. Eluate the column with 20 ml 8 N HNO_3 containing 3 mg/ml NaNO_2 (fresh).
 - 4) The solution is passed through the column. The flow rate is about 1 ml/min.
 - 5) Wash the column with 20 ml 8 N HNO_3 containing 3 mg/ml NaNO_2 .
 - 6) Strip with: 4 ml H_2O , 4 ml 0.3 N NaOH, 4 ml H_2O , 4 ml 2 N HNO_3 , 20 ml 0.5 N HNO_3 containing 0.3 M NaNO_3 .
 - 7) Add 0.3 ml conc. H_2SO_4 . Evaporate to dryness.
6.
 - 1) Dissolve the precipitate with 0.5 N H_2SO_4 . Wash the beaker with 9 ml 0.5 N H_2SO_4 . Combine these solutions into the electrodeposition cell.
 - 2) Adjust the solution to pH = 2.2 for electrodeposition.
 - 3) The current is 0.6 A/cm². The time is 6 h. Cool the cell with water.
 - 4) Cover the surface of the source with VYNS thin film (10-15 $\mu\text{g}/\text{cm}^2$).

3. RESULTS AND DISCUSSION

Seawater samples as large as 200 litres are collected with $\text{Fe}(\text{OH})_2$ coprecipitate at pH = 8.5-9 in a reducing system. The $\text{Fe}(\text{OH})_2$ is dissolved in conc. HCl and conc. HNO_3 . The plutonium is dissolved and leached from possible plankton and solid particles present in the solution. The diluted NaOH (0.5-1 N) is added with a shower to reduce the formation of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. This is of benefit for the plutonium purification. The sample is heated to 400°C for one hour and digested with aqua

regia to destroy the organic material, which may interfere when controlling the valency of plutonium. By the heating, decontamination for polonium is furthermore obtained.



are applied in preparation of Pu^{4+} . The plutonium valences (Pu^{3+}) are reduced to Pu^{3+} by Na_2SO_3 and then, the Pu^{3+} is oxidized to Pu^{4+} by NaNO_2 in 0.5-1 N HNO_3 . Both reactions are fast and nearly quantitative. A high proportion of Pu^{4+} is obtained. Table 1 shows the chemical yield of plutonium using redox-systems of NaNO_2 - NaNO_2 and Na_2SO_3 - NaNO_2 respectively.

Table 1. Comparing the chemical yield of plutonium by redox-systems of NaNO_2 - NaNO_2 and Na_2SO_3 - NaNO_2 respectively.

No.	Seawater litres	Reducing agent	Oxidizing agent	Chemical yield ^{242}Pu , %
165	50	NaNO_2	NaNO_2	24.0
197	200	Na_2SO_3	NaNO_2	88.6
198	200	Na_2SO_3	NaNO_2	83.6

When NaNO_2 and H_2O_2 are applied in preparation of Pu^{4+} , the Pu^{3+} is rapidly oxidized by NaNO_2 and H_2O_2 ; but the Pu^{3+} are rather slowly reduced to Pu^{4+} by NaNO_2 and H_2O_2 . When the H_2O_2 is used to prepare Pu^{4+} , the decontamination for uranium is furthermore inefficient. This is shown in Table 2.

Table 2. Comparing uranium decontamination in seawater using H_2O_2 and NaNO_2 respectively.

No.	Seawater litres	Agent	^{238}U (Bq/m ³)	^{234}U (Bq/m ³)
165	40	5 ml 30% H_2O_2	8.1	9.3
168	50	2 g NaNO_2	0.059	0.63

The anion exchange column is equilibrated with 8 N HNO₃ containing K₂S₂O₈, and 8 N HNO₃ containing fresh NaNO₂ to clean for any impurity in the anion ion exchange in order to prevent any interference.

During washing of the column with 8 N HNO₃ for uranium decontamination, the chem. yield of plutonium is often lost by a change of plutonium valency. In order to keep Pu⁴⁺, the eluate of 8 N HNO₃ containing fresh NaNO₂ is used. When the system is changed from HNO₃ to HCl, the plutonium valence is changed by oxidation of the mixture of HNO₃ + HCl. Therefore, 50 ml conc. HCl containing a few milligram NaNO₂ is used as eluate to prevent the change of the plutonium valence. In Table 3 the chemical yields of plutonium samples are compared when the system is changed to HCl with and without the addition of NaNO₂.

Table 3. Comparing the chemical yield of plutonium by changing the system using 50 ml conc. HCl + few milligram NaNO₂ and 50 ml conc. HCl only.

No.	Volume litres	Agent	Chemical yield ²⁴² Pu, %
197	200	50 ml conc. HCl a few milligram NaNO ₂	88.6
198	200	"	83.6
200	200	50 ml conc. HCl	57.5

Stripping plutonium

We think there are two problems in the plutonium stripping with low acid concentration, i.e. micro-absorption of plutonium and low chemical yield of plutonium. In this work, the plutonium is

successfully stripped with H_2O , NaOH , 2 N HNO_3 , and 0.5 N HNO_3 , containing 0.03 M NaNO_3 . When Pu is stripped with NaOH , the plutonium is hydrolyzed to $\text{Pu}(\text{OH})_3$, leaving the anion exchange resin. Then the $\text{Pu}(\text{OH})_3$ is dissolved in 2 N HNO_3 , and further stripped with 0.5 N HNO_3 , containing 0.03 M NaNO_3 , as a scavenger to prevent the micro plutonium absorption. Table 4 shows the stripping efficiency between 500 ml 0.5 N HNO_3 , + 0.03 M NaNO_3 , (low acid concentration) and H_2O , NaOH , 2 N HNO_3 , 200 ml 0.5 N HNO_3 , + 0.03 M NaNO_3 .

Table 4. The chemical yield of plutonium at the different stripping condition between 300 ml 0.5 N HNO_3 , + 0.03 M NaNO_3 , (low acid concentration) and H_2O , NaOH , 2 N HNO_3 , 200 ml 0.5 N HNO_3 , + 0.03 M NaNO_3 .

No.	Seawater litres	Stripping condition	Chemical yield
			^{242}Pu , %
175	50	300 ml 0.5 N HNO_3 , + 0.03 M NaNO_3	46.9
176	200	300 ml 0.5 N HNO_3 , + 0.03 M NaNO_3	45.0
203	200	H_2O , NaOH , 2 N HNO_3 , 200 ml 0.5 N HNO_3 , + 0.03 M NaNO_3	79.5

Before electrodeposition the sample is heated at 400°C and dissolved in aqua regia for destroying the organic material to get a thin source and for polonium decontamination.

Table 5 and 6 show a comparison of the results obtained by the previous used method and the present one, and Figs. 1 and 2 show sample spectra from the two tables.

Table 5. Plutonium analyses of seawater samples from the North Sea using the old radiochemical procedure. (nd = not detected).

Sample no.	Volume (m ³)	²⁴² Pu-yield (%)	²²⁸ Th (μBq)	²³⁸ Pu (mBq m ⁻³)	²³⁹ Pu (mBq m ⁻³)
870075	0.2	7.6	nd	17.1±19%	nd
870076	0.2	12.6	20±43%	13.0±16%	nd
870077	0.2	9.4	nd	16.4±19%	nd
870078	0.2	7.6	15±33%	7.5±30%	nd
870079	0.2	7.3	76±15%	nd	nd
870080	1.0	41.4	228± 9%	12.5± 7%	0.5±25%
870081	1.8	3.7	nd	12.0±22%	nd
870082	1.8	24.8	nd	15.0± 7%	0.7±16%
870083	1.8	7.2	149±15%	15.3±13%	nd

Table 6. Plutonium analyses of seawater samples from the Danish Waters (Hesselø) using the new radiochemical procedure.

Sample no.	Volume (m ³)	²⁴² Pu-Yield (%)	²²⁸ Th (μBq)	²³⁸ Pu (mBq m ⁻³)	²³⁹ Pu (mBq m ⁻³)
890197	0.2	88.6	nd	7.4± 8%	0.7±35%
890198	0.2	83.6	nd	7.2± 8%	1.7±17%
890201	0.2	72.5	nd	9.0± 8%	2.0±17%
890202	0.2	76.1	-	-	-
890203	0.2	81.9	-	-	-
890205	0.2	72.2	-	-	-

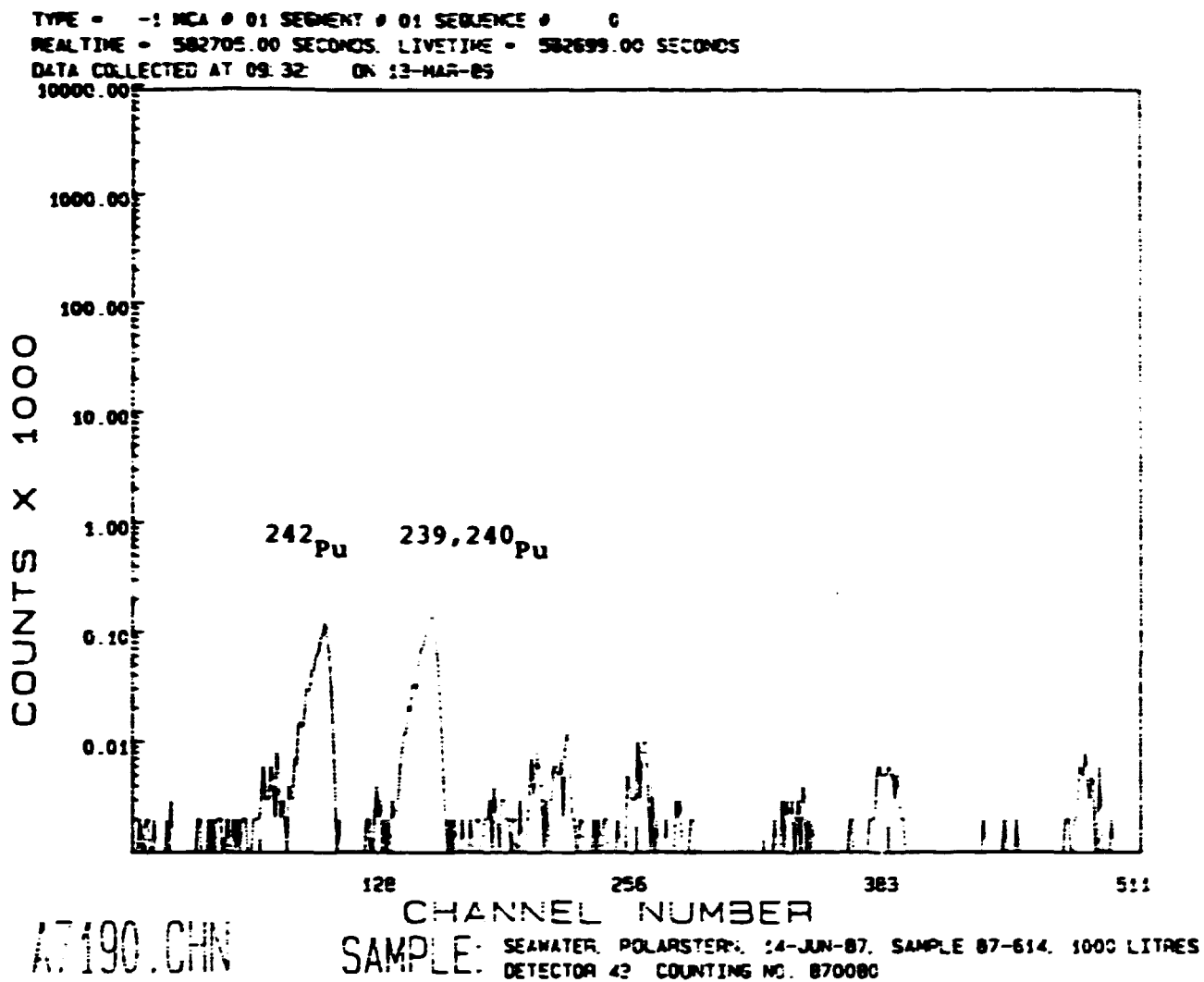


Fig. 1. Sample spectrum (no. 870080) showing thorium contamination (^{224}Th and daughters).

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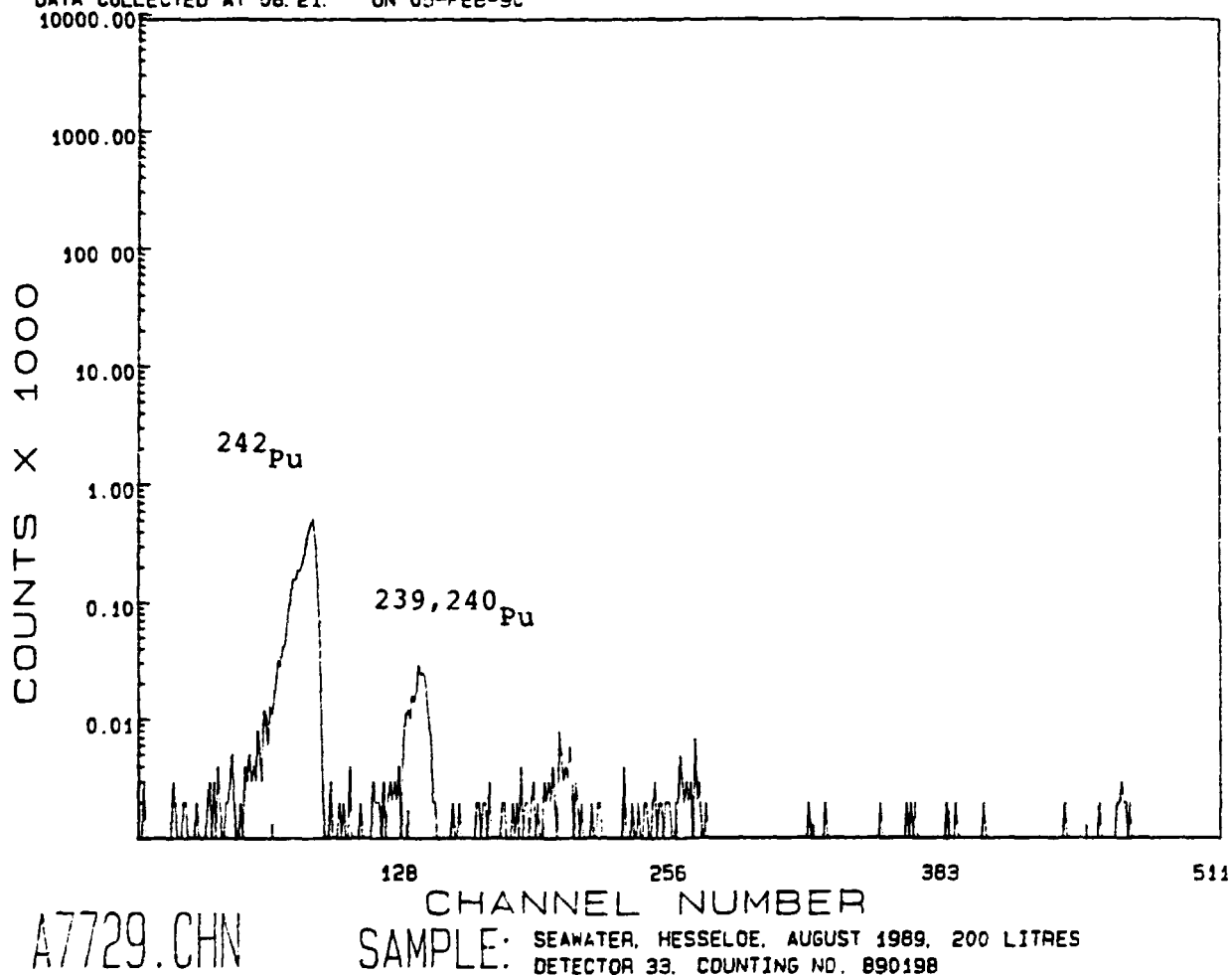


Fig. 2. Sample spectrum (No. 890198) showing no thorium contamination.

4. CONCLUSION

1. Na_2SO_3 and NaNO_2 are successfully applied to prepare Pu^{4+} .
2. The plutonium is stripped from anion ion exchange by H_2O , NaOH , 2 N HNO_3 and 0.5 N HNO_3 + 0.01 M NaNO_3 .
3. With the new procedure we have obtained high decontamination factors for uranium and thorium, high chemical yields (60-80%) for plutonium and high alpha energy resolutions.

APPENDIX 1

Purification of plutonium from disc

1. Put the disc in a 50 ml beaker. Add about 0.5 ml 8 M HNO_3 . Let stand for 1 hour to dissolve. Wash the disc with conc. HCl several times.
2. Wash the disc with 1 .. HNO_3 until clean. Discard the disc.
3. Add 1 ml 1 M NaNO_3 . Evaporate to dryness. Add 3 ml conc. HNO_3 and 3 ml HCl . Heat to dryness.
4. Dissolve with 10 ml 0.7 N HNO_3 . Heat for a few min.
5. Add 300 mg Na_2SO_3 . Stir to dissolve. Let stand for 15 min. The plutonium is reduced to Pu^{+3} valence. (30 mg/ml Na_2SO_3).
6. Add 300 mg NaNO_2 (30 mg/ml). Stir to uniformity. The plutonium is oxidized to Pu^{+4} . Let stand for 10 min.
7. Add 12 ml conc. HNO_3 to get about 8 N HNO_3 .
8. Make a column (7x0.8 cm) AG 1-X₄ 100-200 mesh. Eluate the column with 20 ml 8 N HNO_3 containing 3 mg/ml NaNO_3 (fresh).
9. Add solution to column (0.5 ml/min).
10. Wash the column with 20 ml 8 N HNO_3 containing 3 mg/ml NaNO_2 .
11. Strip with 4 ml H_2O , 4 ml 0.3 N NaOH , 4 ml H_2O , 4 ml 2 N HNO_3 and 20 ml 0.5 N HNO_3 + 0.01 M NaNO_3 .
12. Add 0.3 ml conc. H_2SO_4 . Evaporate to dryness. Add 3 ml conc. HNO_3 and 3 ml conc. HCl . Evaporate to dryness.
13. Dissolve with 5 ml 0.5 N H_2SO_4 . Wash the beaker three times with 0.5 N H_2SO_4 . Each time with 3 ml (transfer to electrodeposition cell). Adjust the pH = 2.2 for electrodeposition.
14. The current is 0.6 A/cm². The time is 6 h. Cool the cell with water.
15. Cover the surface of source with VVNS thin film (10-15 $\mu\text{g}/\text{cm}_2$)

The results of the purification are shown in table 7.

Table 7. After purification, the plutonium chemical yield.

Sample no.	Volume (m ³)	²⁴² Pu-Yield (%)	²²⁸ Th (μBq)	²³⁹ Pu (mBq m ⁻³)	²³⁸ Pu (mBq m ⁻³)
890197	0.2	64.5	nd	7.0±10%	0.88±48%
890198	0.2	65.0	21±37%	7.3±8.9%	1.4±23%
890200	0.2	53.9	19±32%	7.2±9.6%	0.8±38%
8900K1	0.2	58.5	nd	6.4±12.1%	nd
890k2	0.2	66.5	17±43%	8.1±8.8%	0.7±36%

nd = not detected

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<p>Descriptors - INIS</p> <p>ANIONS; CHEMICAL REACTION YIELD; COPRECIPITATION; DECONTAMINATION; HYDROCHLORIC ACID; ION EXCHANGE; IRON SULFATES; LEACHING; NITRIC ACID; PLUTONIUM 239; PLUTONIUM 240; PLUTONIUM IONS; SAMPLING; SEAWATER; SODIUM HYDROXIDES; SODIUM NITRATES; SODIUM SULFATES; THORIUM, URANIUM; VALENCE</p>		
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